Preservation methods throughout the value chain: Fish oil.

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Preservation methods for fish oil

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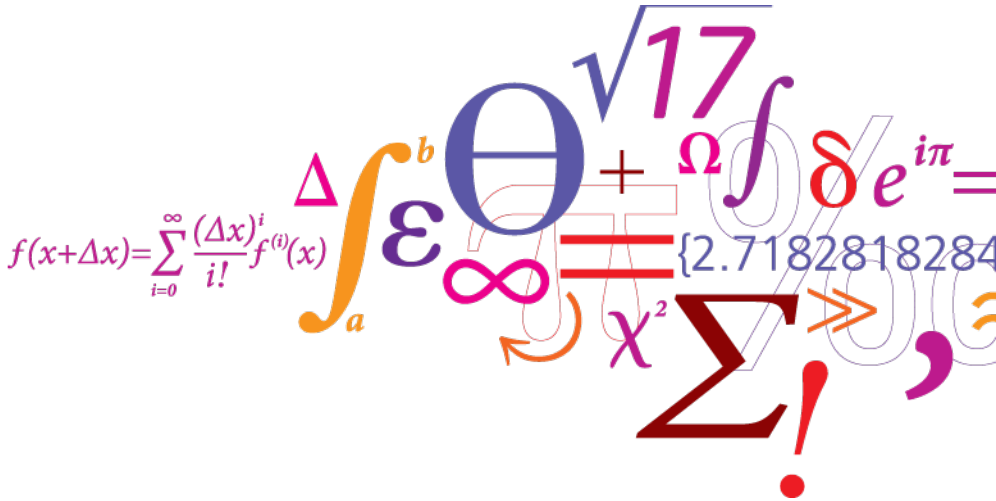

DTU Food
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Agenda

- Intro to antioxidants
- Different examples on effects of antioxidants on fish oil oxidation
  - Tocopherols
  - Citric acid vs tocopherols vs ascorbyl palmitate (AP)
  - Sesamol vs oryzanol vs rosemary extract vs BHT
  - Propyl gallate and citric acid vs rosemary extract and AP
  - Tocopherol and rosemary vs tocopherol
- Research needs

Antioxidants - Mechanisms

Lipidoxidation (Autoxidation)

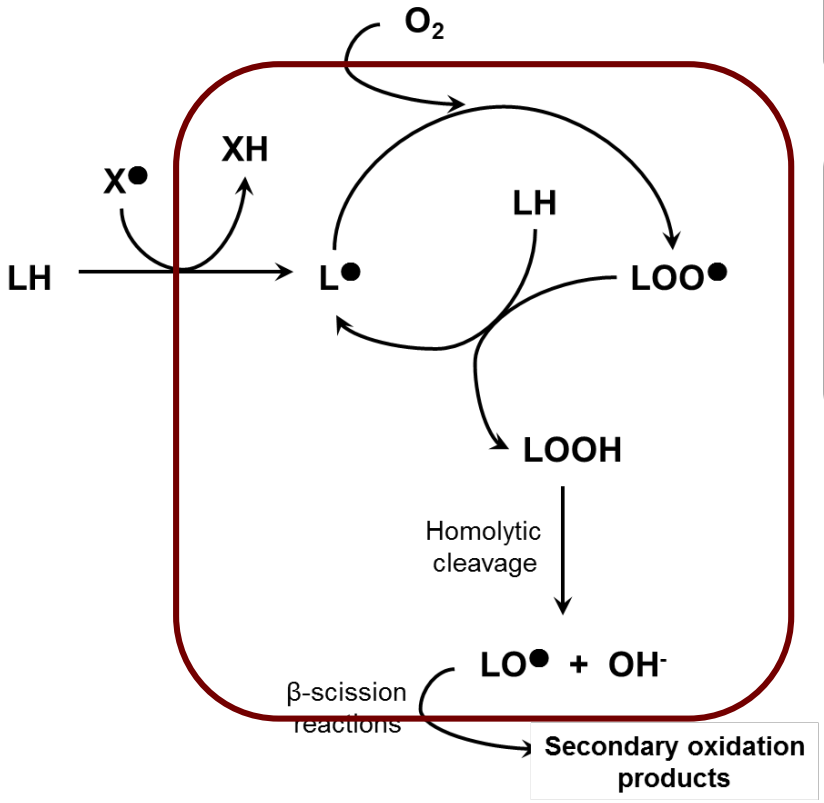


Figure: With courtesy of Ann-Dorit M Sørensen, DTU Food

Primary antioxidants

Radical scavengers

Prevention of initiation and propagation

LOO• + AH → LOOH + A•

LO• + AH → LOH + A•

L• + AH → LH + A•

Termination of lipid oxidation reactions

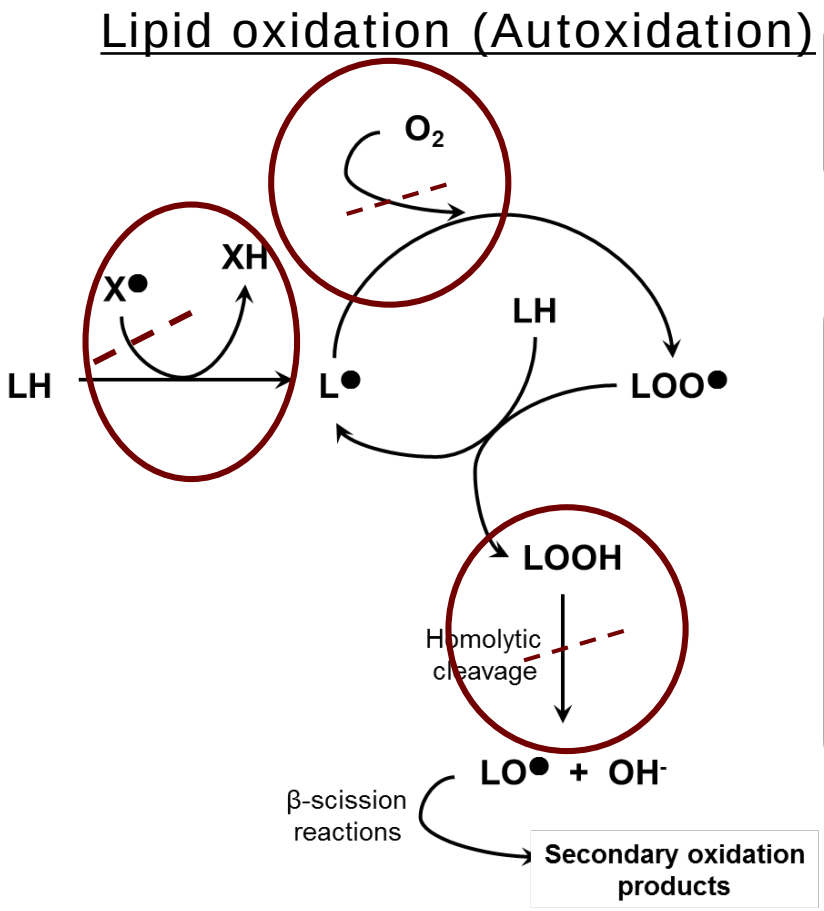
LOO• + A• → LOOA

LO• + A• → LOA

L• + A• → LA

A•+ A• → AA

Antioxidants - Mechanisms



Secondary antioxidants

Metal chelation

Scavenging oxygen

Not illustrated in the figure…

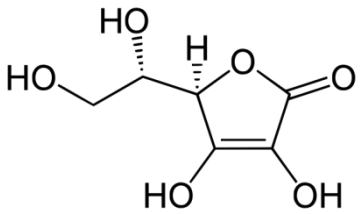
Singlet oxygen quencher

Synergism between antioxidants

Figure: With courtesy of Ann-Dorit M Sørensen, DTU Food

Antioxidants - Mechanisms

Examples on AO which can work as primary or secondary AO



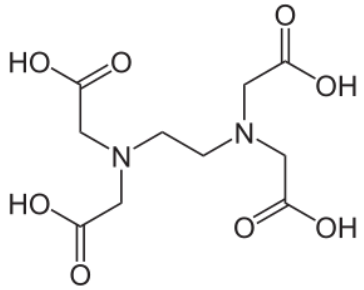
Ascorbic acid

Radical scavenger

Oxygen scavenger

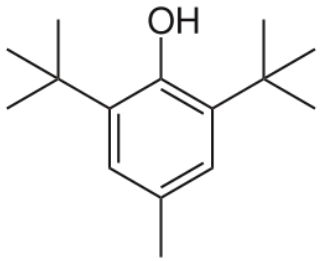
Syngergy with tocopherol

Reducing Fe3+ -> Fe2+



EDTA

Metal chelator

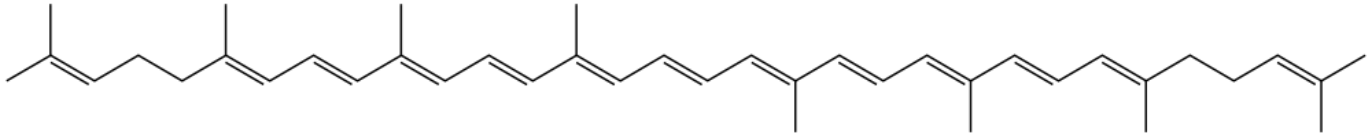


BHT

Radical scavenger

Lycopene

Singlet oxygen quencher

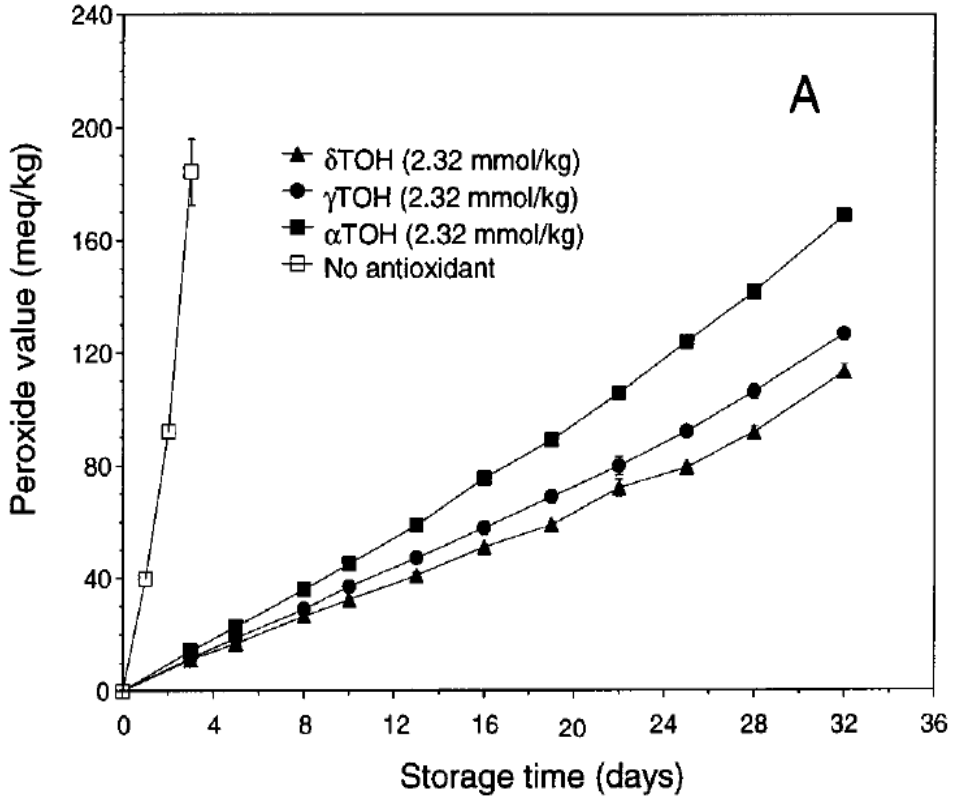


Natural vs synthetic antioxidants

- Synthetic (examples)
  - Propyl gallate
  - BHT
  - Ascorbyl palmitate

- Natural (examples)
  - Tocopherol
  - Ascorbic acid
  - Rosemary extract (rosmarinic acid, carnosol and carnosic acid)
  - Sesamol
  - Oryzanol
  - (Citric acid)

Effect of different tocopherol isomers on and different concentrations on fish oil oxidation (PV and CD) (stripped oils)



Delta- and gamma-toc more efficient than alpha-toc

Kulås and Ackman, J. Agric. Food Chem (2001) 49, 1724-1729

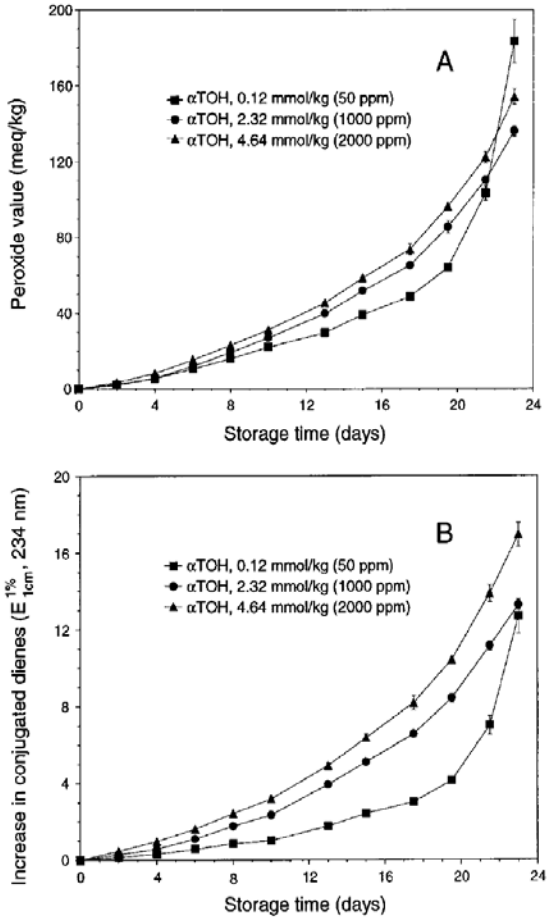


Figure 2. Effect of α-tocopherol (αTOH) on the formation of primary oxidation products in anchovy oil during storage at 30 °C: (A) peroxide value measurements; (B) conjugated diene measurements. Data points are means ± standard deviation, $n = 3$.

Lower concentrations of alpha-tocopherol more efficient than higher ones

Effect of tocopherol homologues on different volatile oxidation products in stripped fish oil

Tab. 2. Values for variables found to be important in the principal component analysis of high-level tocopherol samples*.

PCA variable	αTOH (1000 ppm, day 5)	δTOH (1000 ppm, day 5)
Total volatiles	11.0 ± 0.9 ppm	11.2 ± 0.4 ppm
Hydrocarbons	1.46 ± 0.08 ppm	0.71 ± <0.01 ppm
Propanal	0.37 ± 0.07 ppm	0.70 ± 0.02 ppm
t,c/t,t–2,4-Heptadienal	7.3 ± 1.5**	5.0 ± 0.5***
Diunsaturated/saturated aldehydes	0.61 ± 0.07	0.29 ± 0.04

* The values are mean of two samples ± the difference between the mean and each sample value. Concentrations are relative to the ethyl heptanoate internal standard.
** Day 8: 7.5 ± 0.5 (mean ± standard deviation, n = 3).
*** Day 8: 5.1 ± 0.3 (mean ± standard deviation, n = 3).

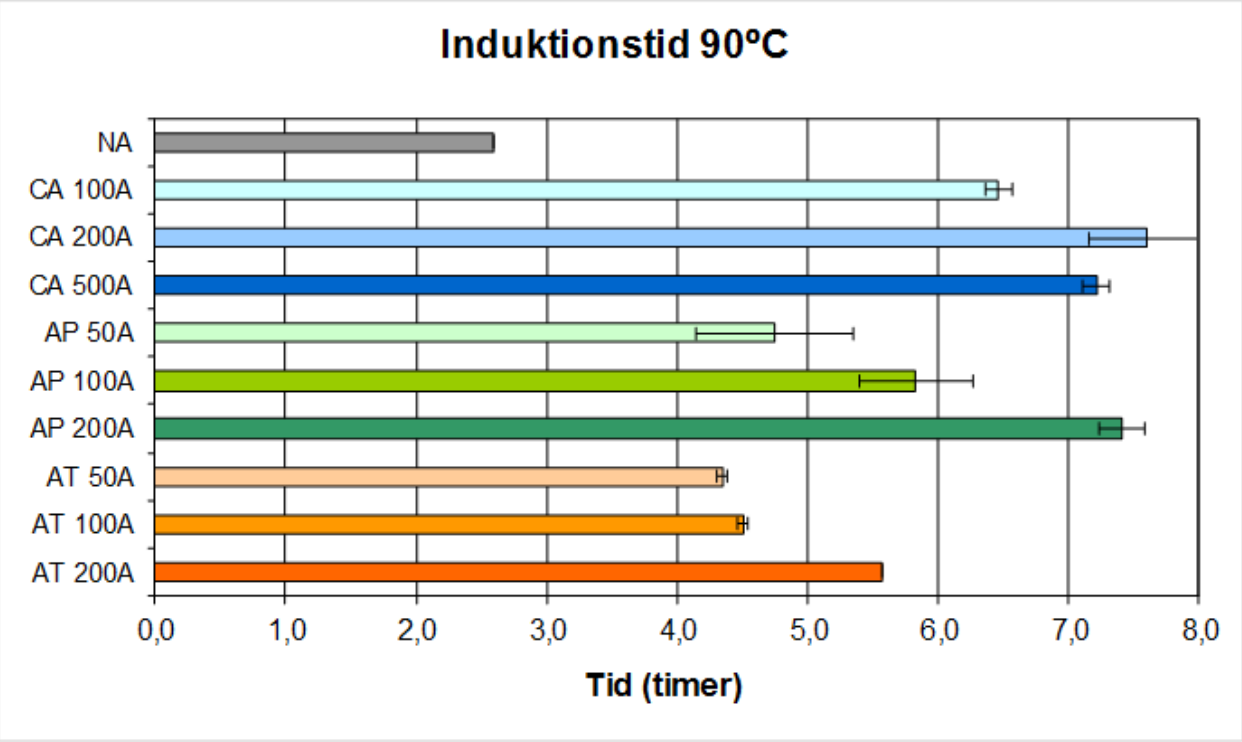
Different tocopherol homologues will change the ratio between different volatiles that are formed

Comparison of the efficacy of citric acid, ascorbyl palmitate and alpha-tocopherol in fish oil by Oxidograph

Oil without antioxidant (NA)

Antioxidants in 3 different concentrations

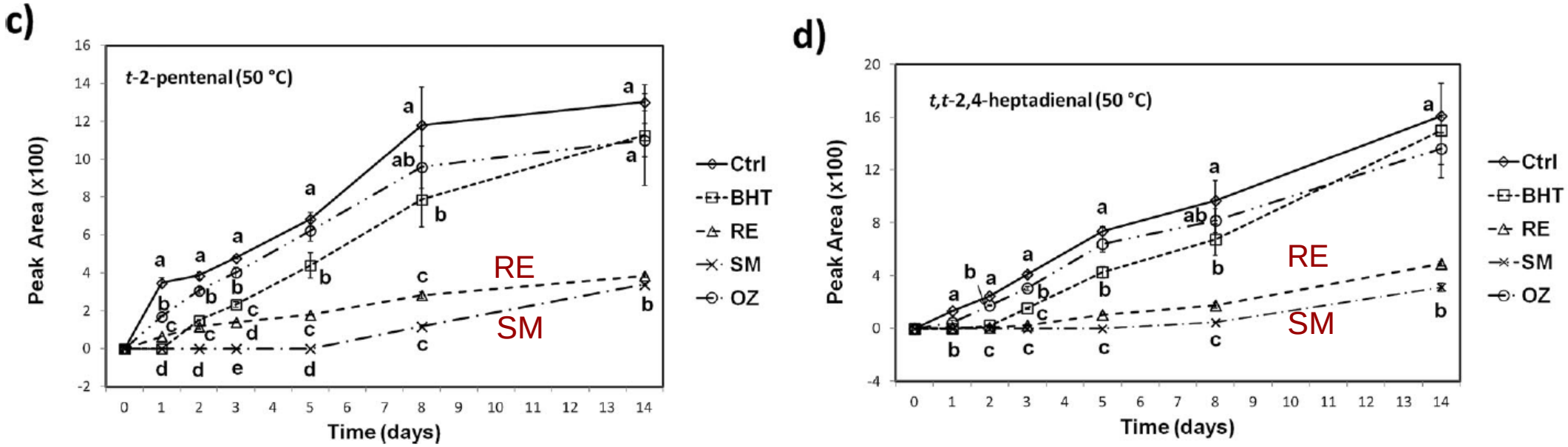
Citric acid (CA), Ascorbyl palmitate (AP) and alpha-tocopherol (AT)



Ascorbyl palmitate and citric acid were equally efficient (200 mg/kg)

Data from DTU Food

Effect of sesamol, oryzanol, rosemary extract or BHT on volatiles in stripped fish oil

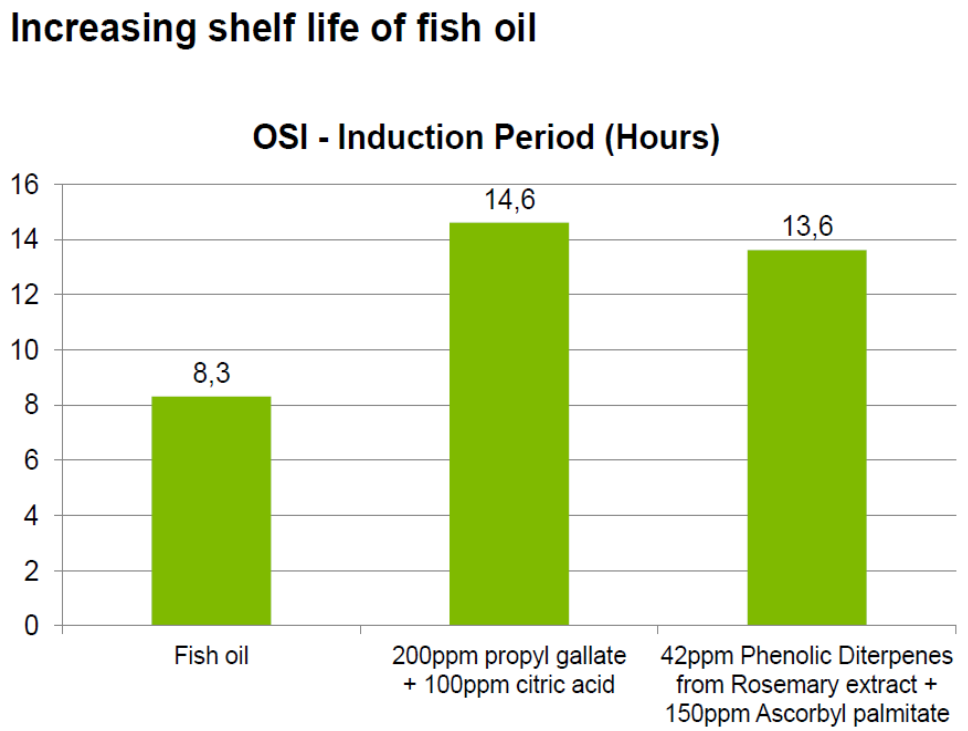


8.4 mM Sesamol SM, Rosemary Extract (RE) or Oryzanol (OZ) vs 0.84 mM BHT

- Rosemary extract and sesamol equally efficient and both better than BHT at 50 ºC
- At 30 ºC, rosemary extract was slightly better than sesamol (data not shown)

Faner et al, EJLST 118, 2016, 885-897

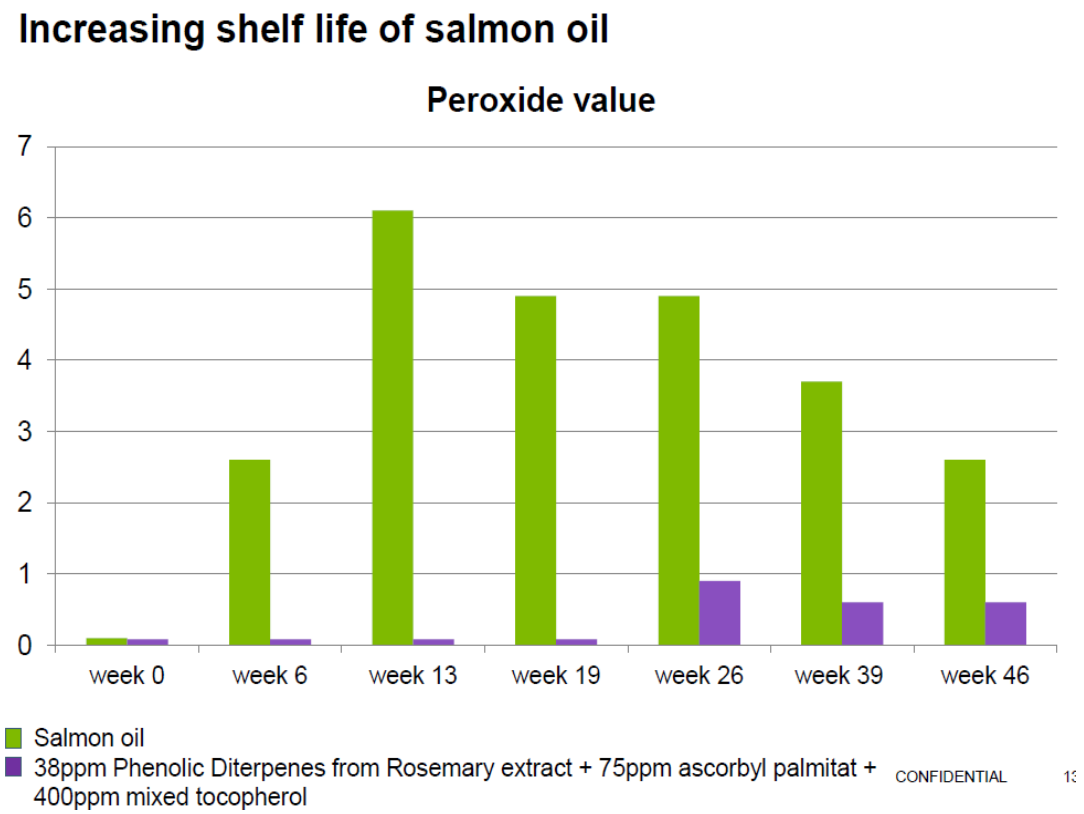
Rosemary and AP vs propyl gallate and citric acid



Rosemary plus ascorbyl palmitate almost as efficient as propyl gallate and citric acid

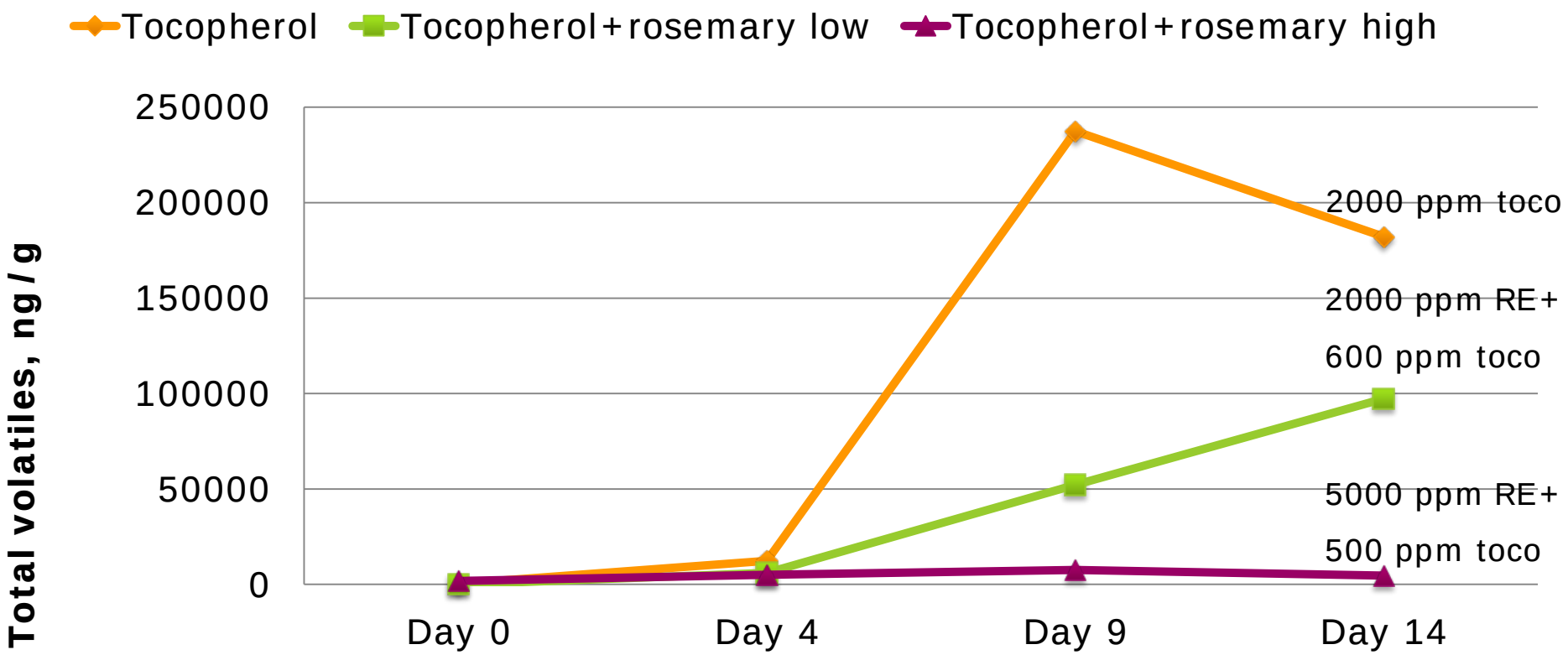
From Dupont presentation Marine Lipider meeting Århus 2014

Rosemary and AP vs propyl gallate and citric acid



From Dupont presentation Marine Lipider meeting Århus 2014

Effect of high concentrations of rosemary and tocopherol on lipid oxidation in fish oil



High doses of rosemary extract and tocopherol almost completely inhibited formation of volatiles

Thomsen et al., Eur. J Lipid Sci. Technol., (2017), 119.

Research needs

- Most studies reported in the literature are carried out with stripped or refined oils

More research should be carried out with unrefined fish oil with different fatty acid compositions and levels of natural antioxidants. Research should address the following questions:

- How can BHT (or ethoxyquin if still used) be replaced by natural antioxidants in unrefined oil?
- Are there differences in antioxidant efficacy in refined vs unrefined oils?
- How is antioxidant efficacy influenced by fatty acid composition and presence of endogenous antioxidants or prooxidants in unrefined fish oils?